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Effect of High-Voltage X-Rays and Cathode Rays on Vitamins (Niacin)

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Effect of High-Voltage X-Rays and Cathode Rays on Vitamins (Niacin)*

Results of extensive tests using three million-volt radiations from Van de Graaff-type generator to irradiate pure solutions of niacin are presented in first report published on subject

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A NUMBER of investigators have shown that X-rays and cathode rays have a lethal effect on microorganisms (*18–20, 24, 30*). The possibility of utilizing X-ray exposures in sterilizing foods was demonstrated by Proctor, Van de Graaff, and Fram in 1943 (*22*). Dunn *et al.* (*7*) found that both X-rays and cathode rays have a lethal effect on a number of bacteria, yeasts, and molds, and they successfully pasteurized milk with the use of cathode rays. If such radiations have potentialities as a means of processing foods, information is essential concerning their effects on vitamins, enzymes, and other nutrients in foodstuffs.

The present paper deals with the effects of hard X-rays and cathode rays produced at three million volts on pure solutions of niacin. The authors know of only three published reports on the quantitative effects of X-rays on vitamins, namely, on ascorbic acid (*1*), *p*-aminobenzoic acid (*25*), and thiamine (*6*). In these instances the investigators used soft X-rays produced at relatively low voltages, 200 kv or less. No published reports have been found on the effect of X-rays on niacin. As compared with soft radiations, the advantage of using high-voltage X-rays is their greater degree of penetration. In other words, as the voltage increases, the wavelength diminishes and the depth to which roentgen rays penetrate matter increases because of the progressive reduction of both the photoelectric and the Compton scattering processes of absorption.

Niacin is a relatively stable molecule. The pyridine ring is noted for its aromaticity and is resistant to oxidation. Information on the oxidation of either pyridine or niacin is lacking. It has been clearly indicated by other investigators, however, that the action of X-rays and cathode rays on other compounds appears to be one of oxidation (*12–14*) or of reduction (*2, 3, 11*), depending on the oxidation-reduction potential. Warburg has shown, by ultraviolet absorption spectra, that it is possible to reduce the niacin in coenzyme II by chemical means (*29*). Ordinary heat processing has little effect on the niacin in foodstuffs (*8*).

Niacin is part of the coenzymes I and II and may have significance from a clinical standpoint in the treatment of cancer.

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* From a paper presented before the Division of Agricultural and Food Chemistry of the American Chemical Society, at its 113th national meeting in Chicago, Illinois on April 19, 1948.

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TABLE 1

Effect of High-Voltage X-Rays on Pure Solutions of U.S.P. Niacin

Concentration.................. 100 γ/ml
Volume irradiated.................. 3 ml
Voltage..................... 3 megavolts

Sample	*Current microamperes*	*Time of Irradiation seconds*	*Dosage*		*Niacin Concentration after Irradiation γ/ml*
			Total roentgens	*Rate r/sec*	
I	230	193	125,000	648	104
G	190	424	250,000	590	104
C	240	545	375,000	688	105
E	240	625	500,000	800	102
F	200	1800	850,000	473	105
L	Control	....	....	...	104*

* Not irradiated

Apparatus

A Trump generator operating at three million volts (*23, 26, 27*), utilizing the pressure-insulated electrostatic principle of Van de Graaff, was used for the production of these radiations. A specially designed X-ray tube was used, which was provided with a window of thin aluminum to close off the tube so that a vacuum could be maintained. Electrons were incident on a water-cooled gold target, 0.25 inch in thickness. The roentgen rays were transmitted in the direction of the electron stream to the sample being irradiated, 3.2 cm below. The X-rays obtained varied in wavelength from 0.004 to 0.06 A.U., with a maximum intensity at 0.008 A.U.

Samples to be irradiated by X-rays were placed in small, cylindrical, stainless steel plates similar to Petri dishes.* These dishes were 0.8 cm high and 2.9 cm in diameter. The covers were 0.5 cm in depth and 3.0 cm in diameter. The dishes were placed in a small adapter, 3.2 cm below the target. The capacity of the dishes was slightly under 3 ml.

For cathode-ray irradiation, the gold target was removed from the path of the electrons. The electrons passed through the thin aluminum window, and cathode rays (beta rays) emerged. The sample was placed in the center of the base of a larger, stainless steel cylinder, 4 inches in diameter, 50 cm below the aluminum plate. The cover of the dish used for cathode-ray exposure was made of thin aluminum and was 0.5 cm high and 3 cm in diameter.

The dosages given are expressed in roentgens, based on ionization of air.

Methods of Assay Used

Niacin was determined photometrically (*16*) in a Cenco Photelometer by a modification of the Mueller and Fox method (*21*) involving the reaction of niacin with cyanogen bromide and ammonium hydroxide. This method was found to be rapid and accurate and to give reproducible results.

Reduced ascorbic acid was determined photometrically, in an Evelyn colorimeter, by the method of Hoch-

* Control tests with glass dishes indicated that the metal containers, which were more convenient to use, played no rôle in the changes observed with niacin during irradiation.

berg, Melnick, and Oser (*17*).

Ultraviolet absorption spectra were determined in a Beckman spectrophotometer. Readings were made at intervals of 5 mμ except at the peaks, in which case the intervals were 1 mμ.

Experimental

Effects of different dosages of high voltage X-rays on niacin in pure solution:

A stock solution of U.S.P. niacin in absolute ethanol containing 100 micrograms of niacin per ml was made and used in this and subsequent experiments. Dilutions were made with distilled water, when necessary.

Niacin concentration 100 micrograms per ml. Samples of the stock solution (3 ml each) were pipetted into the X-ray dishes described above and irradiated for varying periods of time, to obtain total dosages of from 125,000 to 850,000 r (roentgens). After irradiation, the samples were assayed for niacin (Table 1). Ultraviolet absorption spectra were run on an unirradiated control sample and an identical sample irradiated for 850,000 r. Both samples had the same absorption spectra.

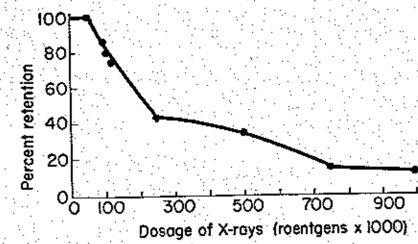

FIG. 1. Effect of different dosages of high-voltage X-rays on retention of niacin in pure solution (50 γ/ml)

Niacin concentration 50 micrograms per ml. Samples (2.5 ml each) of a solution of niacin containing 50 micrograms per ml were pipetted into several exposure dishes and irradiated by X-rays in dosages varying from 50,000 to 1,000,000 r. The irradiated samples and a control sample were then assayed for niacin by the method outlined previously. The irradiation data and the

TABLE 2

Effect of Different Dosages of High-Voltage X-Rays on Pure Solutions of Niacin

Concentration.................. 50 γ/ml
Volume irradiated...............2.5 ml
Voltage.................. 3 megavolts

Sample	*Current micro-amperes*	*Time of Irradiation sec*	*Dosage*		*Niacin after Irradiation*	
			Total roentgens	*Rate r/sec*	*Concentration γ/ml*	*Retention %*
6′	60	85	50,000	589	50.0	100.0
15	60	169	100,000	591	43.0	86.0
1	70	142	110,000	770	40.0	80.0
14	70	157	125,000	795	37.5	75.0
17	260	157	250,000	1591	21.5	43.0
28	220	285	500,000	1755	17.0	34.0
30	250	400	750,000	1875	7.3	14.6
6	230	578	1,000,000	1730	6.0	12.0
G	Control	....	....	....	49.0*	....

* Not irradiated

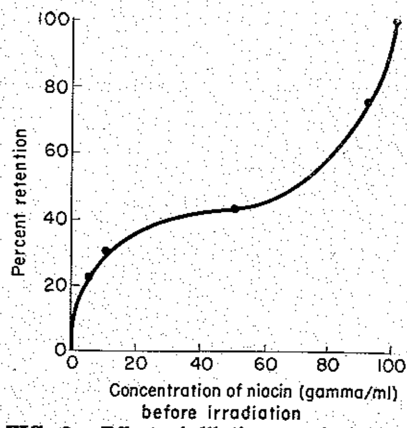

FIG. 2. Effect of dilution on niacin retention after irradiation by high-voltage X-rays (250,000 roentgens)

assay results are presented in Table 2 and depicted graphically in Fig. 1.

Niacin concentration 5 micrograms per ml. In this experiment the concentration of niacin was lowered from 100 to 5 micrograms per ml, and samples were irradiated to the extent of 250,000 r. The results for this dilution are compared in Table 3 and Fig. 2 with those obtained with the higher concentrations of niacin.

Effects of different rates of dosage. To determine whether different rates of X-ray dosage have different destructive effects on niacin when the total dosage is kept constant, 2.5-ml samples of niacin in concentrations of 50 micrograms per ml were irradiated with total dosages of 250,000 r at rates of 295 and 1591 r per sec, and with total dosages of 125,000 r at rates of 177 and 227 r per sec. The data obtained are presented in Table 4.

Effects of different dosages of high-voltage X-rays on niacin in the presence of other compounds:

Forssberg (*10*), Dale (*5*), Tytell and Kersten (*28*), and others have shown that enzymes and organic compounds are "protected" when irradiated by X-rays in the presence of other compounds. The following experiments were conducted to determine whether niacin may be "protected" in a similar manner.

Addition of methionine. Samples (2.5 ml each) of a mixture containing 16 micrograms per ml of methionine and 20 micrograms per ml of niacin and a 2.5-ml control sample of a solu-

TABLE 3

Effect of Dilution on Destruction of Pure Solutions of Niacin by High-Voltage X-Rays

Volume irradiated.............. 2.5 ml*
Voltage.................... 3 megavolts
Total dosage.......... 250,000 roentgens

Sample	*Current micro-amperes*	*Time of Irradiation sec*	*Rate of Dosage r/sec*	*Niacin Concentration* Before Irrad. γ/ml	After Irrad. γ/ml	*Retention of Niacin After Irradiation %*
I	230	193	1294	100	104	100.0
2	230	200	1250	90	64.8	72.0
17	260	157	1594	50	21.5	43.0
1	220	145	1724	10	3.0	30.0
30	230	175	1430	5	1.1	22.0

* Volume of Sample I irradiated was 3 ml

TABLE 4

Effect of Different Rates of Dosage of High-Voltage X-Rays on Niacin in Pure Solutions

Concentration.................. 50 γ/ml
Voltage.................... 3 megavolts

			Dosage		Niacin after Irradiation	
Sample	*Current micro-amperes*	*Time of Irradiation sec.*	*Total roentgens*	*Rate r/sec*	*Concentration γ/ml*	*Retention %*
1	50	708	125,000	177	37.5	75.0
24	100	538	125,000	227	37.5	75.0
4	90	849	250,000	295	21.25	42.5
17	260	157	250,000	1591	21.5	43.0
16	Control	...	....	....	50.0*	....

* Not irradiated

tion containing 20 micrograms per ml of niacin alone were irradiated by 250,000 r. Niacin determinations were made after irradiation. (See Table 5.)

Addition of ascorbic acid. As niacin is a stable molecule chemically and radiobiologically, it was of interest to note what would be the effect of irradiation of a solution of niacin containing ascorbic acid. Therefore, 2.5-ml samples of solutions containing 50 micrograms per ml of niacin and 500 micrograms per ml of U.S.P. ascorbic acid (in 0.5 percent oxalic acid) were irradiated by 125,000 and 250,000 r. Solutions containing 50 micrograms per ml of niacin alone in oxalic acid and 500 micrograms per ml of ascorbic acid alone in oxalic acid were also made, and 2.5-ml samples of these solutions were irradiated by the same dosages. The mixtures were then assayed for niacin and ascorbic acid contents. (See Table 6.)

Ascorbic acid and different quantities of niacin. To determine the minimal amounts of niacin that will "protect" ascorbic acid from X-ray irradiations,

TABLE 5

Effect of High-Voltage X-Rays on Niacin Irradiated in Presence of Methionine

Volume irradiated................ 2.5 ml
Total dosage........... 250,000 roentgens
Voltage.................... 3 megavolts

	Concentration of					Niacin after Irradiation	
Sample	*Niacin γ/ml*	*Methionine γ/ml*	*Current micro-amperes*	*Time of Irradiation sec*	*Rate of Dosage r/sec*	*Concentration γ/ml*	*Retention %*
24	20	16	200	195	1281	4.25	21.2
2	20	..	230	166	1508	5.2	26.0
Control	20	16	...	...	....	20.0*	100.0*

* Not irradiated

TABLE 6

Effect of High-Voltage X-Rays on Solutions of U.S.P. Niacin, U.S.P. Ascorbic Acid, and on Mixtures of the Two

Voltage.................... 3 megavolts
Current.............. 170 microamperes

Sample	Concentration of Niacin γ/ml	Concentration of Ascorbic Acid γ/ml	Time of Irradiation sec	Dosage Total roentgens	Dosage Rate r/sec	Concentration after Irradiation Niacin γ/ml	Concentration after Irradiation Ascorbic Acid γ/ml	Retention after Irradiation Niacin %	Retention after Irradiation Ascorbic Acid %
4	50	500	....	Control	...	50.0*	490.0*	....	....
6	50	500	205	125,000	599	22.0	419.0	44.0	83.8
16	50	....	287	125,000	436	43.0	......	86.0	....
27	..	500	270	125,000	463	...	333.0	....	66.6
15	50	500	542	250,000	462	12.5	392	25.0	78.4
17	50	...	542	250,000	462	20.0	......	40.0	....
1	..	500	500	250,000	453	.....	279	.....	55.8

* Not irradiated

2.5-ml samples of mixtures containing 500 micrograms per ml of ascorbic acid and 33.3, 25, or 10 micrograms per ml of niacin, respectively, were irradiated by 125,000 r. (See Table 7.)

Effect of high-voltage cathode rays on niacin in pure solution:

Different times of irradiation. Four small, stainless steel dishes containing 3 ml of a solution of U.S.P. niacin (100 micrograms per ml) were irradiated by cathode rays produced at 3 million volts and 10 microamperes for 15, 30, 45, and 60 sec. Physical ionization measurements show that irradiation for 60 sec at 10 microamperes is equivalent to approximately 3,400,000 r. Niacin determinations were made after

TABLE 7

Effect of High-Voltage X-Rays on Ascorbic Acid Combined with Different Amounts of Niacin

Voltage.................... 3 megavolts
Current.............. 180 microamperes
Total dosage........... 125,000 roentgens

Sample	Concentration of Niacin γ/ml	Concentration of Ascorbic Acid γ/ml	Time of Irradiation sec	Rate of Dosage r/sec	Concentration after Irradiation Niacin γ/ml	Concentration after Irradiation Ascorbic Acid γ/ml	Retention after Irradiation Niacin %	Retention after Irradiation Ascorbic Acid %
4	33.3	500	163	767	4.6	393	13.8	78.6
6	25.0	500	165	758	3.6	402	14.4	80.4
15	10.0	500	167	749	3.0	392	30.0	78.4

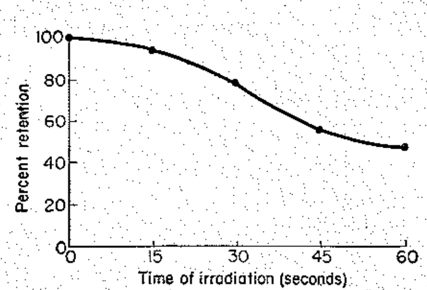

FIG. 3. Effect of high-voltage cathode rays on retention of niacin in solution (100 γ/ml) irradiated at 10 microamperes for different periods

irradiation. (See Table 8 and Fig. 3.)

Dilution effect. To help determine whether the degree of destruction of niacin by cathode rays is more severe in solutions of higher dilution, 3-ml samples of niacin in concentrations of 100, 80, 50, 25, and 10 micrograms per ml were irradiated for 60 sec by cathode rays produced at 3 megavolts and 10 microamperes. Niacin determinations were made after irradiation by the method previously mentioned. (See Table 9 and Fig. 4.)

Effect of high-voltage cathode rays on niacin in the presence of other compounds:

This experiment was designed to determine the relative radiosensitivity of niacin *per se* and in the presence of other compounds. Irradiation for 60 sec with cathode rays at 10 microamperes was carried out on 3-ml samples of solutions, with the results shown in Table 10.

Discussion of Results

Effect of high-voltage X-rays on niacin:

U.S.P. niacin in a concentration of 100 micrograms per ml was not destroyed by X-rays in dosages up to 850,000 r.

When the concentration of niacin in the solution was reduced to 50 micrograms per ml or less, partial destruction was apparent with dosages of 100,000 r or above. The degree of destruction was apparently exponential, as may be seen in Fig. 1.

A similar effect of dilution was noted when solutions of niacin in concentrations ranging from 100 to 5 micrograms per ml were irradiated for 250,000 r.

Niacin is apparently more radiosensitive in dilute solutions than in concentrated solutions. This finding

TABLE 8

Effect of High-Voltage Cathode Rays on Solutions of U.S.P. Niacin

Concentration . . . . 100 γ/ml
Volume irradiated . . . . 3 ml
Voltage . . . . 3 megavolts

Sample	*Current micro-amperes*	*Time of Irradiation seconds*	*Niacin after Irradiation* Concentration γ/ml	*Niacin after Irradiation* Retention %
G	Control	0	100*	100*
E	10	15	94	94
C	10	30	79	79
I	10	45	55	55
F	10	60	46	46

* Not irradiated

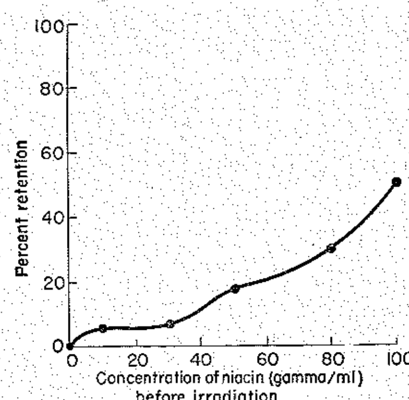

FIG. 4. Effect of cathode rays produced at 10 microamperes for 60 seconds on solutions of niacin of varying concentrations

resembles a radiation phenomenon observed by Dale (*4*) with carboxypeptidase, by Forssberg (*9*) with catalase, and by others.

The results strongly suggest that destruction of niacin by X-rays is the result of indirect action of the radiations on the solvent rather than of direct destruction of the niacin by "hits." The theory is based on the premise that most of the molecules of the solute that react to the radiations have not been excited or ionized directly by the radiations but their reaction follows the ionization of the solvent molecules. In the early literature, this reaction is referred to as "activated water." This theory is in direct contrast to the "hit" or "target" theory or "Treffer Theorie," whereby the molecule or structure in which ionization is produced is designated as the "target" and the production of ionization as a "hit."

If the theory of indirect action, with the production of an intermediary body of finite life, is to be applied to vitamins, there should be a competitive reaction for this intermediary body when a vitamin is irradiated in the presence of another solute. Such has been shown to be the case with catalase by Forssberg (*10*), with carboxypeptidase by Dale (*4*), with acetylcholine by Dale

TABLE 9

Effect of High-Voltage Cathode Rays on Solutions of Niacin of Different Concentrations

Voltage.................. 3 megavolts
Current............. 10 microamperes
Irradiation............... 60 seconds

Sample	*Concentration of Niacin* *Before Irradiation* γ/ml	*After Irradiation* γ/ml	*Retention of Niacin* %
C	100	51.0	51.0
I	80	23.8	29.7
G	50	8.8	17.6
E	25	1.6	6.4
F	10	0.6	6.0

TABLE 10

Effect of High-Voltage Cathode Rays on Niacin Alone and on Niacin in the Presence of Other Compounds

Voltage.................... 3 megavolts
Current............... 10 microamperes
Irradiation................. 60 seconds*

	Concentration before Irradiation		*Niacin after Irradiation*	
Sample	*Niacin* γ/ml	*Other compounds*† γ/ml	*Concentration* γ/ml	*Retention* %
G	50	50 G	8.75	17.5
E	42.8	12.9 M	8.75	20.4
F	66.7	33.3 G	13.75	20.9
G′	50	50 C	3.75	7.5
I′	50	50 C′	5.50	11.0
Control 1	50	......	8.75‡	17.5‡
Control 2	40	......	14.0‡	10.0‡
Control 3	66.7	......	14.0‡	21.0‡

* Sample E was irradiated for 62 seconds
† G = glycine; M = methionine; C = cystine; C′ = cysteine · HCl
‡ Not irradiated

(5), and with urease by Tytell and Kersten (28).

When niacin was irradiated in the presence of methionine, the data show that methionine competed with niacin for the ionized particles, but the niacin was slightly more reactive with the activated water and "protected" the methionine. The difference in niacin destruction when niacin alone was irradiated and when niacin combined with methionine was irradiated was not great enough, however, to justify sweeping conclusions.

When niacin in combination with ascorbic acid was irradiated by 125,000 and 250,000 r, the results were unexpected. Although ascorbic acid is a more labile molecule than niacin and was more labile to X-rays when irradiated alone, when the two combined were irradiated by X-rays, the niacin was destroyed more readily than the ascorbic acid. Hence ascorbic acid appears to be protected by niacin. One may assume that niacin competes with ascorbic acid for the activated water particles in this instance. Niacin in concentrations of as little as 10 micrograms per ml protected 500 micrograms per ml of ascorbic acid from X-rays.

Reference to the previous tables indicates that the rate of dosage of X-rays was not the same in all instances, which presents the possibility that the results obtained might be ascribed to this fact. Accordingly an experiment was conducted in which solutions of niacin of a given concentration were irradiated by X-rays for total dosages of 250,000 and 125,000 r, respectively, each total dosage being delivered at two different rates. This was accomplished by changing the current. For the total dosage of 125,000 r the second of the two rates of dosage was increased 30% over the first rate, and for the total dosage of 250,000 r, 440%. The data show that at a given total dosage the net results in niacin destruction were the same, irrespective of the difference in the rates of dosage, even when this difference was as much as 440%.

Effect of high-voltage cathode rays on niacin:

Cathode rays produced at 10 microamperes for as short a period as 15 seconds were destructive to niacin in pure solution, even at a concentration of 100 micrograms per ml. Hence cathode rays may accomplish in a few seconds what it takes X-rays minutes to do.

In no case of cathode or X-ray irradiation in this investigation was any noticeable heat produced in the samples. This is to be expected, for in an X-ray beam of 1 sq cm there is produced but 10^{-3} to 10^{-5} calorie per sec (15).

The amount of destruction of niacin by cathode rays increased with dilution, as in the case of X-rays. Therefore, it would seem that the action of cathode rays on niacin is indirect.

Curves for the ultraviolet absorption spectra of solutions of niacin (100 micrograms per ml), irradiated for 45 and 60 seconds by high-voltage cathode rays at 10 microamperes, are presented in Fig. 5. Irradiation, which resulted in a loss of niacin as represented by the cyanogen-ammonia reaction, also resulted in a slight shift in the absorption maximum as compared with the absorption maximum of nonirradiated niacin, namely, from 262 to 263 mμ. The minimum changed from 238–239 to 241 mμ. When niacin was irradiated, the optical density increased from 270 mμ on. These data confirm the assay results and, furthermore, may offer some possible means of detecting what happens to the niacin molecule upon irradiation, for microchemical methods are not feasible with such small quantities. Further work on this is in progress.

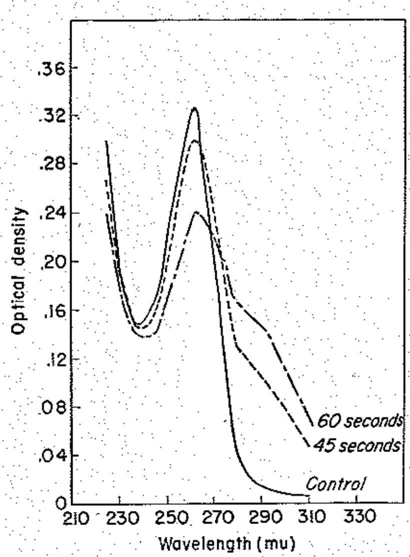

FIG. 5. Effect of high-voltage cathode rays on ultraviolet absorption spectrum of niacin in solution (100 γ/ml) irradiated for 45 and 60 seconds at 10 microamperes

Methionine protected niacin from cathode rays. There was a 20% retention of niacin when it was irradiated in the presence of methionine and only a 10% retention when niacin was irradiated alone. Glycine offered no protection to niacin from cathode rays. There was a greater destruction of niacin when it was irradiated in the presence of cysteine or cystine than when irradiated alone by cathode rays.

Summary and Conclusions

1. Pure solutions of niacin were irradiated by X-rays and by cathode rays produced at 3 megavolts, and the degree of retention of niacin after irradiation was measured.

2. Niacin in a concentration of 100 micrograms per ml was not destroyed by X-rays in total dosages between 125,000 and 850,000 r.

3. When the concentration of niacin was reduced to 50 micrograms per ml, partial destruction of the vitamin occurred at X-ray dosages between 50,000 and 100,000 r.

4. The percentage destruction of niacin of this concentration was increasingly greater with increasing dosages of X-rays between 50,000 and 250,000 r, but at greater dosages the destruction decreased, percentagewise, until it reached a constant level at dosages between 750,000 and 1,000,000 r.

5. When the total X-ray dosage was 250,000 r, the percentage destruction of niacin was greater for greater dilution of vitamin, but the increased destruction was not linear with the dilution.

6. The effect produced on niacin by a given total dosage of X-rays was independent of the rate of dosage up to at least five times the initial rate.

7. When niacin was irradiated by X-rays in the presence of methionine, niacin loss was slightly greater than that when niacin was irradiated alone.

8. Niacin in the presence of ascorbic acid was destroyed by hard X-rays more readily than niacin irradiated alone, although the ascorbic acid alone was more radiosensitive than the niacin alone. In the presence of niacin, ascorbic acid was less radiosensitive to hard X-rays.

9. Ascorbic acid (500 micrograms per ml) was protected from hard X-rays by as little as 10 micrograms per ml of niacin.

10. High-voltage cathode rays had a destructive effect on niacin in a concentration of 100 micrograms per ml in as short a period of irradiation as 15 seconds at 10 microamperes.

11. Increased time of exposure of niacin in this concentration to cathode-ray irradiation at 10 microamperes resulted in increased destruction of the niacin. The rate of destruction was not linear, however, with the time of irradiation.

12. Dilution of the niacin solutions irradiated by high-voltage cathode rays had the same effect on the retention of niacin as was noted in the case of X-ray irradiation of dilute solutions. The relationship between the dilution and the retention of niacin was not linear, but at low concentrations was asymptotic.

13. There was a greater retention of niacin when it was irradiated by cathode rays in the presence of methionine than when it was irradiated alone. The reverse held true when niacin was irradiated with cysteine and cystine.

14. The action of both hard X-rays and cathode rays on niacin appeared to be indirect.

15. Irradiation of niacin by cathode rays resulted in a change in the ultraviolet absorption spectrum.

* * *

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